

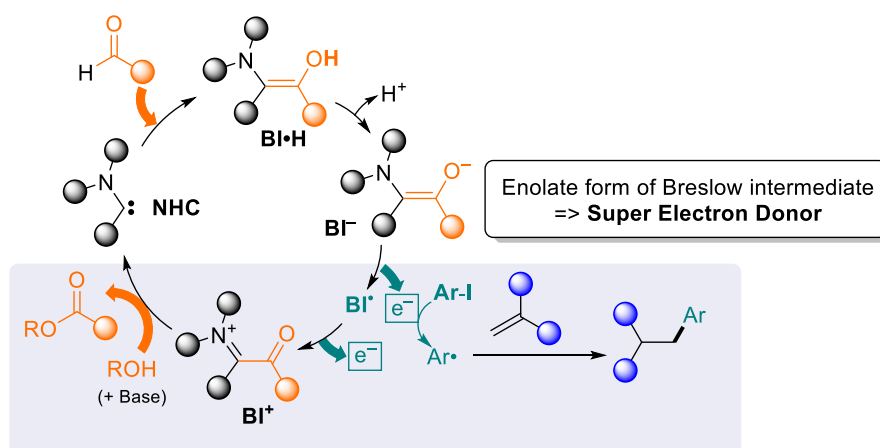
A simple *N*-Heterocyclic carbene for the catalytic conversion of aldehydes into Super Electron Donors

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NHCs have been widely used in organocatalysis for the oxidation of aldehydes *via* the formation of the so-called Breslow intermediate. Until recently, the fate of the electrons lost during these oxidative transformations had not been addressed. In 2021, Ohmiya and Bertrand independently demonstrated that these Breslow intermediates can also be used as formal reductants.^{[1][2]} NHC-catalyzed arylacylations of diverse alkenes were thus performed by reducing iodoaryl derivatives into radical species. In their redox neutral process, the aldehyde used to generate the Breslow enaminol was also incorporated into the final addition product, affording ketone derivatives.

In this new study, our objective was to develop a strategy where the Breslow enolate catalyst serves both as an electron source for challenging reductive transformations and as a key intermediate for the valorization of aldehydes through oxidative transformations. We focused on novel sources of NHCs and aldehydes to generate more powerful Organic Electron Donors (OEDs).^{[3][4]} Imidazolylidene-based enaminols proved to be powerful donors for the single-electron transfer reduction of various challenging substrates. This method also enabled the interdependent formation of two distinct products. The reduced radical intermediates were exploited in the arylation of alkenes, while the sacrificial aldehydes were valorized through concomitant oxidation reactions.^[5]



Scheme 1- Proposed mechanism for NHC-catalyzed concomitant oxidative and reductive transformations

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